

PREPARATION OF FIBROUS REINFORCED SAUSAGE-TYPE CASINGS  
FROM POLYVINYL ALCOHOL RESINS

ABSTRACT OF THE DISCLOSURE

A novel fibrous casing for packaging sausages and similar products comprises a fibrous web impregnated with a continuous film of an insolubilized, film-forming polyvinyl alcohol resin. The casing is preferably prepared by impregnating a suitable saturating tissue with dissolved or heat-softened polyvinyl alcohol resin and then insolubilizing and setting the resin as a film on the tissue, e.g., in the case of dissolved resin, by contacting with a coagulation (acid, salt, or non-solvent liquid) bath or by evaporation of the solvent, and, in the case of heat-softened resin, 10 by cooling. Further insolubilization of the resin film may be effected by reacting the resin with a suitable cross-linking agent, viz. formaldehyde. Resin impregnated-saturating tissue may be formed directly into a tubular casing or initially may be produced as a sheet which is slit to appropriate width and then formed into a tubular casing in a separate seaming operation. Casings are preferably formed using long fiber hemp papers as the saturating tissues and the particular film-forming polyvinyl alcohol resins best adapted to the preparation technique employed.

PREPARATION OF FIBROUS REINFORCED SAUSAGE-TYPE CASINGS  
FROM POLYVINYL ALCOHOL RESINS

This invention relates to new and improved sausage-type casings and the methods of preparing the same. More particularly, the invention is concerned with the preparation of casings for packaging sausages and similar products using film-forming polyvinyl alcohol resins. The invention is primarily directed to the production of novel fibrous casings comprising a tubular insolubilized polyvinyl alcohol resin film reinforced with a fibrous web of saturating tissue, preferably a long fiber hemp paper tissue.

10 Natural casings are prepared from the intestines of various edible animals, primarily cattle, hogs, and sheep. The intestines are removed from the slaughtered animal and thoroughly cleaned by processes well known in the art. Natural casings, which have been thoroughly cleaned, are stuffed with various sausage meat compositions and formed into sausage links in preparation for cooking.

Prior to about 1925, substantially all sausage casings were natural casings prepared from animal intestines. Since that time, there have been developed several types of synthetic sausage casings. Some artificial sausage casings are prepared by reconstitution of a tubular film from animal hide fibers to yield a tough collagenous film. The major proportion of artificial casings, however, are prepared from regenerated cellulose, preferably by the viscose process, although some casings are manufactured by the cuprammonium process and also by denitration of extruded cellulose nitrate tubes.

30 There has been a considerable consumer acceptance of pre-sliced sausages, such as bologna, salami, etc., which are sold in the form of relatively small conveniently sized packages, each package containing a small predetermined quantity of sausage in the form of a fixed number of slices. The reason for this is that the slicing of the sausage is performed mechanically, thus yielding

a product of uniform thickness for ease of packaging. In order to provide a predetermined number of slices in a package of a given weight, it is essential that the diameter of the sausage be carefully controlled. In the preparation of sausages by the meat packer, a sausage emulsion is inserted into the sausage casing which is subsequently tied off at each end and cooked or cooked and smoked. In order to assure uniformity of size of the sausage slices, casings are provided to the trade known as fibrous casings. Fibrous casing is composed of cellulosic fibers, preferably in the 10 form of a saturating tissue paper, which are impregnated and held together by regenerated cellulose. The paper used, preferably a long fiber hemp paper, is impregnated with viscose, formed into a tube, and treated in a coagulating and regenerating bath to regenerate cellulose within and upon the paper. The product is a fiber reinforced regenerated cellulose casing having relatively high strength and relatively low stretch.

Over a period of many years, cellulose casings have remained the most desirable and generally the most economical, in spite of the development of competing, cheaper plastics, because 20 cellulose has properties of strength, both wet and dry, low stretch, and permeability to moisture vapor and smoke, which are required in the processing of sausage products. For example, some plastics, such as polyethylene, polyvinyl chloride, etc., which are easy to process in film form have never produced satisfactory sausage casings because of a deficiency in smoke or moisture vapor permeability. On the other hand, most other common plastic packaging films, including polyvinyl alcohol, while having the advantage of being easily formed into films which have a high moisture vapor and smoke permeability are too stretchy, 30 particularly when wet, for use in forming sausage casings. For polyvinyl alcohol films, for instance, a stretch of up to 700% at break load, when wet, is typical.

STATEMENT OF OBJECTS AND FEATURES OF THE INVENTION

It is, therefore, one object of this invention to provide a new and improved sausage casing constituting a fibrous-reinforced polyvinyl alcohol resin film and a method of preparing the same.

Another object of this invention is to provide a new and improved polyvinyl alcohol resin sausage casing having high strength and low stretch under rewet conditions.

Another object of this invention is to provide a new and improved method for preparing polyvinyl alcohol resin sausage casings by impregnation of a saturating tissue fibrous web with an aqueous or organic solution of a film-forming polyvinyl alcohol resin.

An additional object of this invention is to provide a new and improved method for preparing polyvinyl alcohol resin sausage casings by impregnation of a saturating tissue fibrous web with a melt-extruded film of polyvinyl alcohol resin.

A feature of this invention is the provision of a new and improved sausage casing comprising a tubular, fibrous-reinforced, insolubilized polyvinyl alcohol resin film.

Another feature of this invention is the provision of a new and improved method for the direct preparation of fibrous-reinforced sausage casing by coating and impregnating a saturating tissue, preferably a long fiber hemp paper, formed into a tube with either an aqueous or organic solvent solution or a heat-softened extruded film of a film-forming polyvinyl alcohol resin and insolubilizing and setting the resin as a dry continuous film in and on the tissue tube.

Another feature of this invention comprises a new and improved method for the preparation of fibrous sausage casing wherein a saturating tissue is impregnated with either an aqueous or organic solvent solution or a heat-softened extruded film of a film-forming polyvinyl alcohol resin, the resin is insolubilized and set as a dry continuous film in and on the tissue and the

resultant coated tissue subsequently is formed into a tube.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

#### SUMMARY OF THE INVENTION

This invention comprises a new and improved sausage casing and method of preparing the same. A web of a saturating tissue, preferably a long fiber hemp paper, is impregnated and coated with either an aqueous or organic solvent solution or heat-softened 10 melt-extruded film of a film-forming polyvinyl alcohol resin and the impregnated and coated web is suitably treated to insolubilize, set, and, where applicable, dry, the polyvinyl alcohol resin as a continuous film. Further insolubilization of the deposited resin by reaction with a cross-linking agent, such as formaldehyde, preferably also is carried out. The cross-linking agent may be incorporated in the impregnating resin solution or melt or brought into contact with the impregnated tissue in a separate treating step. The polyvinyl alcohol-impregnated web directly may be in the form of a tubular casing at the time of impregnation or may be 20 initially produced as a sheet which then may be cut to desired width size with the resultant narrower widths being formed into tubular casings by a suitable adhesive seaming step. The resultant tubular casings may be given a final curing or moisture equilibration treatment. The necessary and optional steps of the method of the invention are set forth as solid and dotted lines, respectively, in the diagrammatic flow sheet illustrated in Fig. 1.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow diagram broadly showing typical alternative steps used in the method of the invention,

30 Fig. 2 is a diagrammatic view showing the continuous coating of a fibrous web and formation of the same into a casing using a polyvinyl alcohol resin solution in accordance with this invention,

Fig. 3 is a diagrammatic view showing another embodiment of the method of the present invention for the continuous coating of a fibrous web and direct formation of the same into a tubular casing using a polyvinyl alcohol resin solution,

Fig. 4 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web on a knife over roll coater,

Fig. 5 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web using a floating doctor blade coater,

Fig. 6 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web using a continuous blanket knife coater,

Fig. 7 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web in a reverse roll coater,

Fig. 8 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web in a contra-coater,

Fig. 9 is a diagrammatic view showing the application of a polyvinyl alcohol resin solution to a fibrous web in a three-roll, direct roll coater,

Fig. 10 is a diagrammatic view showing the continuous coating and impregnation of a fibrous web with melt-extruded polyvinyl alcohol resin and direct formation of the same into a casing in accordance with this invention, and

Fig. 11 is a diagrammatic view showing another embodiment of the method of the present invention wherein a fibrous web as a sheet is initially coated and impregnated with melt-extruded polyvinyl alcohol resin and the resultant film-impregnated sheet subsequently is formed into a tubular casing.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to new and useful improvements in sausage casings. In the preferred embodiments of this invention,

a suitable heat-softened, melt-extruded or dissolved film-forming polyvinyl alcohol resin is appropriately impregnated in and coated as a continuous film upon a fibrous web of saturating tissue, preferably a long fiber hemp paper.

Vinyl alcohol, as a monomer, is not known to exist. All attempts to prepare vinyl alcohol have resulted in the rearrangement of the compound to acetaldehyde. Commercially, polyvinyl alcohol resins normally are prepared by hydrolysis of vinyl polymers containing vinyl aliphatic or aromatic ester units, including 10 vinyl polymers such as polyvinyl ester homopolymers, e.g., polyvinyl acetate, polyvinyl propionate, polyvinyl benzoate, etc.; and carboxylated polyvinyl ester polymers, e.g., those produced by copolymerizing a vinyl ester such as vinyl acetate, vinyl propionate, and vinyl benzoate with an ethylenically unsaturated carboxylic acid such as acrylic acid, methacrylic acid and maleic acid. The extent of the hydrolysis is controlled to produce products having the desired hydroxyl group degree of substitution. Polyvinyl alcohol resins so produced and useful in the present invention have a D.S. with regard to OH group content of at least 20 about 20% and usually in the range of from about 40% to about 99.99%, the latter figure approximating the maximum hydrolysis efficiency attainable in commercial practice. In the case of resins containing carboxyl groups, the invention broadly contemplates the use of those having a D.S. with regard to carboxyl functionality ranging up to about 25%, preferably in the range of from about 0.1-10%.

For purposes of this invention, it is necessary to use polyvinyl alcohol resins which are film-forming (e.g., D.P. is at least about 800). Such resins, as is known, typically have a 30 viscosity of at least about 4 centipoises, e.g., in the range of from about 4 to about 65 centipoises and above, as 4% by weight aqueous solutions at 20°C. as conventionally measured on an Ostwald-Fenske Viscometer. Such properties are necessary to

provide a suitable impregnation of the fibrous saturating tissue web while also providing adequate strength and resistance to moisture to the insolubilized and dried film. In general, solubility decreases while film strength and melting point increase with increasing polyvinyl alcohol resin molecular weight and OH group content. Resins having an OH group D.S. above about 95%, for example, while less soluble and higher melting, form films which are quite resistant to moisture even without cross-linking. Cross-linking, however, does render such and other resins stronger 10 and less sensitive to water and, accordingly, cross-linking of the resin in the film is preferred in the present invention.

In embodiments of the present method wherein the resin impregnation step of the process is carried out by contacting and saturating a fibrous web with a solvent solution of polyvinyl alcohol resin, the solvent in the resin solutions utilized in the present invention suitably may be any aqueous or organic liquid in which the particular polyvinyl alcohol resin being employed is soluble (e.g., capable of forming viscous solutions useful herein containing 1-40% by weight polyvinyl alcohol resin). Specific 20 solvents preferred for use in given instances depend primarily on the particular polyvinyl alcohol resin employed.

For example, polyvinyl alcohol resins having a lower OH group D.S., e.g., those having a D.S. not exceeding about 80%, have a wide range of solubility in organic solvents, including solubility to varying degrees in anhydrous organic liquids such as alcohols, e.g., methanol, ethanol, and isopropanol; ethers, e.g., the monomethyl, monoethyl, monobutyl, and diethyl ethers of ethylene glycol and diethylene glycol; ketones, e.g., acetone, methyl ethyl ketone, diacetone alcohol, methyl isobutyl ketone, 30 and cyclohexanone; esters, e.g., ethyl acetate, methyl acetate, and n-butyl acetate; chlorinated compounds, e.g., carbon tetrachloride and ethylene dichloride; hydrocarbons, e.g., benzene and toluene; nitro-compounds, e.g., nitrobenzene; and heterocyclic

compounds, e.g., dioxane and tetrahydrofuran, as well as in water-containing miscible liquid mixtures comprising members of said organic liquids. In this latter respect, it will be understood that the phrase "organic solvent" as employed herein embraces miscible mixtures of water and organic liquids containing sufficient levels of organic liquid to modify any solubility characteristics that water displays alone, e.g., when at least 10% by volume of the total solvent is organic. Moreover, at such lower OH group D.S. levels ranging up to about 80%, polyvinyl alcohol 10 resins are soluble in aqueous alkaline media. Preferred embodiments of such alkali soluble resins for use in the present method by virtue of the improved overall properties of films formed thereby are those having an OH group D.S. of at least about 40%.

On the other hand, as stated, as the OH group content of the resin increases, resin solubility in general and in hydrophobic liquids, in particular, decreases. Resins of higher OH group D.S., e.g., above about 80%, thus, while soluble to a lesser extent in the above-described organic solvents, more advantageously are dissolved with aqueous solvents, the more hydrophilic organic 20 solvents, viz. alcohols, and mixtures thereof. Water is a particular preferred solvent for such resins having an OH group D.S. of at least about 98%. Especially useful organic solvents for these and other such high OH group resins include miscible alcohol-water mixtures having a volume ratio of alcohol:water of at least 0.4:1 and wherein the alcohol is a low molecular weight alkanol, such as methanol or ethanol.

The heat sensitivity of the polyvinyl alcohol resins is another factor which affects solvent selection. It is, of course, desired to avoid having to use elevated temperatures and/or vacuum 30 pressure conditions in finally drying impregnated web produced in the process. Hence, in the embodiments of the invention using a solvent vehicle to impregnate the fibrous web, a solvent preferably is utilized which is a normally volatile liquid, e.g., a

liquid having a boiling point (760 mm Hg) not exceeding about 100°C.

In accordance with embodiments of the present invention utilizing a solvent vehicle in the web impregnation step thereof, the polyvinyl alcohol resin solution may be applied to the web by any of a variety of well known coating techniques. In general, resin solution application is effected by continuously passing a web (e.g., in an upward, downward, or horizontal direction) past and in contact with a suitable resin solution applicator means.

10 The impregnated and coated fibrous web, as stated, may be formed directly into tubular casings or the resultant sheets may be later formed into casings through a seaming operation. In either case, the applied polyvinyl alcohol copolymer is insolubilized on the fibrous web by an effective treatment and then optionally may be, and preferably is, further insolubilized by reaction with a suitable cross-linking agent.

Although the invention broadly embraces the use of any convenient technique which is effective to insolubilize the polyvinyl alcohol resin in and on fibrous webs coated and impregnated with 20 the solvent solutions of the resin, the preferred embodiments typically utilize one of several techniques wherein resin insolubilization is effected mainly by a removal of solvent from the resin solution-impregnated web. One such approach involves displacing solvent from the solution-impregnated web by passage of the impregnated web through a coagulation bath in which the polyvinyl alcohol resin is regenerated. The compositions of preferred coagulation baths vary for particular systems depending upon the given resin and solvent employed but generally include either aqueous or organic solutions of acids, salts, and mixtures thereof 30 (e.g., sulfuric acid, ammonium sulfate, and combinations thereof) or organic liquids (i.e., nonsolvents) in which the particular resin employed is partially soluble or insoluble and which effect

coagulation of the resin. For example, coagulation baths comprising acidic highly concentrated aqueous salt solutions, such as sulfuric acid-containing concentrated ammonium sulfate solutions, are especially useful in regenerating polyvinyl alcohol resins from aqueous solutions thereof. Particularly useful for coagulating polyvinyl alcohol resins from organic solvent solutions, e.g., alcohol-water solutions, are regeneration baths comprising a "nonsolvent" (e.g., acetone or benzene) which is more organophilic than the organic solvent.

10 In other preferred embodiments of the invention wherein impregnation of the web with resin is via a resin solvent vehicle and in particular in those utilizing normally volatile solvents, insolubilization of the resin is effected by evaporation of the solvent. Volatile liquid-containing polyvinyl alcohol resin films blister at elevated temperatures. Accordingly, evaporation of the solvent preferably is effected at moderate temperatures, e.g., on the order of 100°-120°C., although higher temperatures can be employed if contact time is short. Reduced pressures can be utilized if necessary or desirable. By choosing a suitably 20 volatile solvent, however, the need for using vacuum conditions can be eliminated. Heating of the resin-impregnated web can be effected directly or indirectly by convection, radiation, or any other available conventional heating technique. Typically the desired heating is carried out by contacting the web with a heated inert gas such as air.

In applying the polyvinyl alcohol resin to fibrous webs via a solvent solution thereof, it is preferred to provide a cross-linking agent which will react with the deposited polyvinyl alcohol during drying and heat curing to produce a film upon and 30 within the fibrous web which is insoluble in and relatively insensitive to water. In one preferred technique, a suitably soluble cross-linking agent is incorporated into the resin solution applied to the web and becomes activated during the drying

treatment. It is also possible to initially apply the polyvinyl alcohol resin solution and then by means of a spray, bath, or other conventional application technique using the same or a different solvent as used for the polyvinyl alcohol resin, separately apply the cross-linking agent to the resin-containing film. Particular cross-linking agents contemplated to be applied to insolubilize the polyvinyl alcohol resin in the present invention include the conventional agents well known to be capable of forming cross-links between molecules of polyvinyl alcohol resins. Specific 10 examples of such materials which contain two or more reactive functional groups per molecule include aldehydes, such as formaldehyde, glutaraldehyde, glyoxal, etc.; polymethylol derivatives, such as water-soluble formaldehyde-amine and formaldehyde-amide condensation products, e.g., dimethylol urea, trimethylol melamine, and liquid urea-formaldehyde resins; diisocyanates, such as the diisocyanate of dimerized linoleic acid, 4,4'-methylene bis (cyclohexyl isocyanate), etc.; diisothiocyanates, such as the diisothiocyanate of dimerized linoleic acid, 4,4'-methylene bis (cyclohexyl isothiocyanate), etc.; polyepoxides, such as butadiene diepoxide 20 and the like; polyamide epichlorohydrin resin; acyl halides, such as adipoyl chloride, sebacyl chloride, etc.; and polymeric ketenes, such as the diketene of dimerized linoleic acid. In applying the cross-linking agents to insolubilize polyvinyl alcohol resin, the less reactive cross-linking agents may be applied in admixture with the solution of polyvinyl alcohol resin. In the case of more reactive cross-linking agents, the polyvinyl alcohol resin may be applied to the fibrous web and subsequently treated with the cross-linking agent in a separate treating step, preferably prior to drying and curing. Where necessary or desirable, a catalyst for 30 the cross-linking agent may be added to the system via the resin solution, the cross-linking agent stream, a separate stream, etc.

In embodiments of the present method wherein impregnation of the fibrous web is carried out using a melt-extruded polyvinyl

alcohol resin, the film-forming polyvinyl alcohol resins preferred for use are those having a D.S. of OH groups of at least about 60%. In the case of such melt-extrudable resins containing carboxyl groups, a maximum of a D.S. with regard to carboxyl functionality of about 5% is preferred, and more preferably the maximum is about 0.5%. Resins having such characteristics are suitably extrudable into films for impregnating the fibrous saturating tissue web and form ultimate films in and on the web having desired strength and moisture resistance properties. In general, as 10 stated, solubility goes down while film strength increases with increasing molecular weight and OH group content. Film-forming resins having an OH group D.S. above about 95%, for example, can be extruded, when suitably plasticized, into films which are quite resistant to moisture even without cross-linking. As in the case of solvent deposited film, cross-linking, however, does render such and other melt-extrusion resins deposited stronger and less sensitive to water and, accordingly, cross-linking of the resin in melt-extruded and deposited films is also preferred in the present invention.

20 On the other hand, extremely high molecular weight polyvinyl alcohol resins may present difficulties since resin melting point rises with increasing resin molecular weight. The preferred polyvinyl alcohol resins for use have melting points below about 220°C., e.g., in the range of from about 180° to about 215°C. Such resins typically have a D.P. in the range of from about 1000 to about 5000 and display a viscosity as 4% aqueous solutions, measured as described above, of less than about 45 centipoises. The more preferred of such resins furthermore are substantially uniform polymers, completely melting within a 10°C. temperature 30 range.

Extrusion of the polyvinyl alcohol resins into films in the present invention requires that the resin be suitably and effectively plasticized. This allows extrusion to be carried

out at temperatures below those at which the resin is thermally degraded (e.g., above about 240°C.) and also at melted resin viscosities which provide self-supporting, yet fibrous web-impregnating, extruding films. Preferred impregnation results, more specifically, may be obtained by effectively plasticizing the polyvinyl alcohol resin to produce at normal shear rate melt viscosities in the range of from about 100 to about 10,000 poises.

In general, any component or mixture of substances which display a plasticizing action on polyvinyl alcohol resins are 10 suitable for use as the plasticizer ingredient in the resins extruded in the present invention. The more effective polyvinyl alcohol resin plasticizers usually are humectant, water-soluble monomeric or polymeric alcohols, amines, or amides. Specific examples of suitable plasticizers include, without limitation, glycerol, ethylene glycol, propylene glycol, polyethylene glycols and polypropylene glycols having a molecular weight up to about 1000 (triethylene glycol, tripropylene glycol, Carbowax\* 200, Carbowax\* 400, Carbowax\* 600, etc.), trimethylol propane, sorbitol, formamide, urea, and polyoxyethylene ethers and esters containing 20 from about 2 to about 20 moles of ethylene oxide per molecule, e.g., monophenyl ethers of polyoxyethylene containing 2-7 ethylene oxide units per molecule (e.g., Pycals\*), furfuryl alcohol ethers of polyoxyethylene containing 3-12 moles of ethylene oxide per molecule, and similar ethyloxylated derivatives of urea (Nopco\* GS-5), dimethyl formamide, trimethylol propane, etc. The more preferred plasticizers, such as the described polyoxyethylene derivatives, are those having normal (at 760 mmHg) boiling points above about 220°C.

The amount of plasticizer utilized in particular embodiments varies depending primarily upon the resin to be extruded 30 and the extrusion conditions. Increased plasticizer levels in general are required with increasing resin molecular weight and lower extrusion temperatures and pressures. To produce suitable

melt viscosities in the above described range, typical plasticizer levels are in the range of from about 5% to about 40%, more usually from about 15% to about 30%, by weight of the polyvinyl alcohol resin. Higher or lower plasticizer loadings may be employed, however, providing the resultant mixture is extrudable into self-supporting, substantially non-tacky films.

Due to the relatively high temperatures employed in the extrusion step in the present method, it is preferred that water (and other volatile substances) be essentially excluded from the 10 resin mixtures to be extruded. When present in appreciable quantities, the water and similar volatile materials flash off, causing surface defects to be formed in the extruded film as it leaves the die. The more preferred embodiments, hence, select or pre-treat starting resin, plasticizer components, etc., to maintain moisture levels in resin mixture feeds to the extruder below about 0.5%, total weight basis.

In accordance with the present invention, plasticized polyvinyl alcohol resin may be heated and extruded into film and the film applied to a reinforcing fibrous web by any of a variety of 20 well known techniques. The nature of the extrusion device is not critical and any extrusion device designed and adapted to melt-extrude thermoplastic resins into films suitably can be used in the present invention. Typically, the operation is continuous and, in general, entails extruding a flat or tubular resin film having a temperature above the transition point of the resin, guiding the film into impregnating contact with a saturable fibrous web, and lowering the temperature of the resultant so placed resin to result in the web being impregnated and coated with a continuous enveloping film of the resin. By initially 30 forming the fibrous web into a tube and appropriately extruding the polyvinyl alcohol resin as a web-impregnating tubular film, tubular casings, as stated, may be formed directly in the present invention. In other instances, the extrusion and web-impregnation

operations initially form only a flat sheet constituting the fibrous web impregnated and coated with a continuous polyvinyl alcohol resin film. The resultant flat sheets then are formed into tubular casings in a seaming operation using an adhesive for polyvinyl alcohol resins, such as aqueous and organic solvent solutions of polyvinyl alcohol resins, diisocyanates, epoxides, and the like.

Impregnation of the fibrous web by melt-extruded polyvinyl alcohol resin in the present invention results from the extruded 10 polyvinyl alcohol resin film being maintained above the second order transition (i.e., softening) temperature of the particular resin (e.g., typically 5-10°C. below the melting temperature) until after it has been guided into the desired envelopment of the web. Some cooling of the extruded film, such as by contacting it with cooler fluids (e.g., air) or cooler surfaces (e.g., chilled plates or rolls) is, however, contemplated for use and, indeed, may be preferred in embodiments utilizing the more elevated extrusion temperatures.

The necessary guiding of the extruded film in and onto the fibrous web can be accomplished by a variety of means. One approach entails passing a continuous web, while supporting it, closely adjacent the die from which the resin film is being extruded. The polyvinyl alcohol resin is directly extruded onto the web under sufficient pressure to effect the desired impregnation. This technique may be used, for example, to impregnate and coat fibrous web initially formed into a tube to directly produce casing by the present method.

In another approach, the desired placement of the extruded film may be achieved by extruding a polyvinyl alcohol resin film 30 at a point removed from a fibrous web, guiding the web and softened resin film together so that their flat surfaces are in surface-to-surface contact, and then applying sufficient pressure, such as by passing the contacting web and film through an appropriately

constricted opening defined between two spaced rigid members (e.g., the nip of two oppositely rotating rolls), to press the resin film into and through the fibrous web. This method usually is employed to produce resin-impregnated flat sheets which are subsequently converted into tubes, although it also can be employed in direct casing production.

Embodiments of the latter type immediately above are exemplified by the use in the present invention of modifications of the process broadly disclosed in U.S. Patent No. 2,958,364. In 10 such approaches a fibrous web is formed into a tube and passed to within the interior of a supporting, open-ended, usually cylindrical, mandrel. A tubular film of polyvinyl alcohol resin is formed within the interior of the fibrous web tube by conventional blow melt-extrusion techniques. Impregnation of the fibrous web by the resin film is effected by proper application of pressure, e.g., by maintaining the internal pressure within the blow-molded resin bubble at sufficiently high levels through an air line positioned in the die and communicating an outside source of variable air pressure with the interior of the film bubble.

20 After a fibrous web is impregnated with melt-extruded resin in accordance with the present method, the polyvinyl alcohol resin is cooled to temperatures below the second order transition point of the resin to set (i.e., insolubilize) the resin in the form of a continuous film enveloping the reinforcing web. The rate at which the deposited resin cooling may vary although it must be at least sufficiently rapid and immediate enough after contact of the web by the hot resin to prevent undesirable thermal degradation of the web material. The deposited resin cooling suitably can be carried out by indirect or direct means using any convenient cooling expedient including cooled inert fluids such as air or water, chilled surfaces, the fabric web itself, and combinations thereof. The desired cooling of the impregnated web may be effected in a treating zone in common with or separate from the zone in which

impregnation of the web with extruded film is carried out. For example, one preferred resin cooling approach involves utilizing a chilled surface (or surfaces) to support or press the fibrous web during the resin film impregnation step whereby resin cooling is simultaneous with resin film impregnation.

As stated above, the polyvinyl alcohol resin-impregnated fibrous webs produced in accordance with the present invention may be, and preferably are, treated with a cross-linking agent which will react with and cross-link the polyvinyl alcohol resin 10 in the film during autogenous or heat curing of the coated article to render the film upon and within the fibrous web more insoluble in and then less sensitive to water and other solvents. Where employed, the cross-linking agent can be applied in any conventional manner. A typical embodiment utilizes an aqueous or organic solution of a cross-linking agent and by means of a spraying, bathing, or other conventional coating technique applies the solution to a reinforcing web prior to resin impregnation and/or to a resin-impregnated web before or after the described resin-setting cooling step. Alternatively, a slow-reacting cross-linking agent 20 such as an epoxide resin may be added to the system via the resin feed to the melt extruder and later triggered after formation of a resin-impregnated web by contacting the product with a suitable catalyst/accelerator (e.g., ammonia for an epoxide) for the cross-linking reaction.

Particular cross-linking agents contemplated to be applied to further insolubilize the polyvinyl alcohol film resin in embodiments of the present invention wherein melt-extrusion is employed to apply the resin to the fibrous web include any bi- or poly-functional agents capable of forming cross-links between molecules 30 of polyvinyl alcohol resins described above with respect to the resin solution web application technique of the invention. Where necessary or desirable, a catalyst, accelerator, and the like for the cross-linking agent may be added to the system via the resin

melt, the cross-linking agent stream, a separate stream, etc. After the desired application of a cross-linking agent to or completion of a cross-linking agent/accelerator combination on the resin film, the resultant resin in the film then is cured to introduce cross-linkages and insolubilize the resin. Although curing at room temperature often is effective, heating preferably is utilized during the curing step to shorten treating time. Heating may be useful also to set a seaming adhesive, where one is employed, or to remove solvents used as vehicles for adhesives, 10 cross-linking agents, etc.

In preparing casings in accordance with this invention, it is preferred to use a fibrous web comprising a saturating tissue formed of long hemp fibers bonded together with a suitable wet strength sizing agent, such as regenerated cellulose or an insolubilized polyvinyl alcohol resin of high OH group D.S., i.e., greater than about 80%. Other nonwoven webs, such as Yoshino paper, rice paper, paper formed of polyvinyl alcohol resin fibers, hemp, rayon, cotton and nylon; and woven fabrics such as muslin, marquisette, cheese cloth, organdy, and voile can be used. It 20 should be understood that these fibrous webs are commercially available. The long fiber hemp paper (Dexstar paper) is generally preferred for reasons of maximum strength, ease of handling, and economy.

#### APPARATUS AND PROCESS FOR CASING PREPARATION

Referring to Fig. 2 of the drawings, there is shown a diagrammatic view of an apparatus which can be used for coating or impregnating a fibrous web with a solution of a polyvinyl alcohol resin and directly forming the same into a fibrous casing in accordance with this invention.

30 In Fig. 2, a ribbon of paper 11, preferably of the type described in U.S. Patent No. 2,045,349 which is a long fiber hemp paper weighing in the range from 12-16 pounds per ream, depending upon the size and weight of casing being manufactured, passes from

roll 12 over rollers 13 and 14 and around formers 15 and 16 which form the paper into tubular form. The paper formed into a tube, then proceeds downwardly over a mandrel 17. Mandrel 17, which is preferably a hollow metal tube, e.g., a steel pipe, having an outside diameter of 2-7 inches, more or less, depending upon the size of the tube or casing which is to be produced, may be of any suitable length, conveniently about 30 feet long, and, as shown, can be suspended from a suitable support such as an I-beam 18 or the like. The paper 11, now shaped in the form of a tube, passes 10 downwardly over mandrel 17, through a forming ring 19 which is preferably a metallic ring having an inside diameter only slightly larger than the diameter of the tube shaped paper passing through it and whose purpose it is to maintain the paper in tubular form until it reaches the coating die 20. Coating die 20 is essentially a hollow ring structure made of metal or the like and contains an annular opening 21 circumferentially of its inside diameter through which an aqueous or organic solvent solution of polyvinyl alcohol resin, which is contained under positive pressure in the chamber of the die 20, is applied to the outer surface of the downwardly 20 moving paper tube to uniformly impregnate and coat it with polyvinyl alcohol resin solution. The polyvinyl alcohol resin solution is prepared in a mixing tank and supplied to a holding tank from which it is introduced to the die as indicated diagrammatically in Fig. 2.

A sleeve 33 is formed of metal or the like which is shrunk onto mandrel 17 functions to effect a more uniform application of polyvinyl alcohol resin solution through the orifice 21 as the paper tube 11 passes downwardly thereover. A number of slip rings 22 which may be shrunk onto the mandrel 17 at suitable intervals, 30 e.g., three feet, and which are made of metal or the like, function to keep the inside wall of the polyvinyl alcohol resin coated and impregnated paper tube from scraping against the outside wall of mandrel 17 as the tube moves downwardly.

In the embodiment of the invention depicted in Fig. 2, the apparatus is arranged with mandrel 17 extending through a dryer chamber 23. Dryer chamber 23 is provided with a hot air inlet 24 supplied with air from heater 25 by means of high capacity fan or pump 26. Dryer 23 is effective to produce a rapid preliminary drying of the polyvinyl alcohol resin coated and impregnated fibrous casing.

From the lower end of dryer 23, the dried fibrous casing is collapsed and passes through rolls 27 positioned at the inlet 10 28 to dryer 29. Dryer 29 is also provided with a pair of rolls 31 adjacent outlet 30 therefrom. Rolls 27 and 31 are effective to trap a "bubble" of air in the casing to maintain it under a desired inflating pressure to prevent the casing from shrinking during drying. Dryer 29 may be supplied with heated air from an alternate heater, not shown, or may be supplied with heated air from air heater 25 as indicated in dotted line. In preparing casing in accordance with this embodiment of the invention, the polyvinyl alcohol resin-impregnated fibrous tube is dried thoroughly in dryer 23 and is cured in dryer 29. The casing is re-humidified to a desired moisture level either by introduction of moist air at the outlet end of the dryer or by subjecting the casing leaving the dryer to storage under moisture equilibration conditions. Solvent vaporized from the casing in dryers 23 and 20 29, where desired, may be condensed and recovered for reuse and recirculation in the system in a conventional solvent recovery unit shown diagrammatically in Fig. 2.

In Fig. 3, there is shown a diagrammatic view of another embodiment of the present invention for coating and impregnating a fibrous web with a solution of a polyvinyl alcohol resin and 30 directly forming the same into a fibrous casing. The apparatus shown there, at least with regard to the means for forming the paper into a tube and applying the coating and impregnating resin solution, is identical to that of Fig. 2 and, correspondingly,

like elements in the tube-forming and solution-coating means of the two apparatus are numbered the same.

In Fig. 3, as in Fig. 2, a ribbon of paper 11, preferably a long fiber hemp paper is fed from roll 12, formed into tubular form around formers 15 and 16, passed downwardly over mandrel 17 and past coating die 20 where an aqueous or organic solvent solution of polyvinyl alcohol resin is applied to the outer surface of the downwardly moving paper tube to uniformly coat it with said resin solution.

10 In Fig. 3, mandrel 17 extends into container 123 which contains a coagulating bath 124, e.g., aqueous or organic liquid bath containing a coagulating concentration of an acid, salt, or organic nonsolvent liquid for the resin, for insolubilizing and regenerating a polyvinyl alcohol resin film within and upon the fibrous web. The mandrel 17 may be provided with an inlet pipe or conduit 125 and an outlet pipe or conduit 126 for conveying coagulating liquid into and out of the interior of the tubular casing formed in the apparatus. The inside flow of coagulating liquid is at a rate sufficient to maintain a liquid level within 20 the formed tube which is approximately equal to the level of bath 124 in container 123.

At the bottom of container 123 there is provided a roller 127. The casing is flattened in the bottom of the container 123 and passes around roller 127 and out of the coagulation and regeneration bath. Casing 128 (as distinguished from the untreated paper 11 at the inlet end of the process) passes out of the coagulation bath and over a series of rollers which guide it into and out of a series of treating baths. Containers 130 and 140 through which the casing is guided contain additional coagulating liquid 30 131 and 141, respectively, to ensure complete insolubilization of resin in the casing. From container 140 the casing is passed through tank 150 which contains a quantity of wash liquid 151 for washing out coagulating liquid and any by-product materials from

the casing. In tank 160 the casing is contacted with a bath 161 containing a plasticizer (e.g., glycerol) and a cross-linking agent (e.g., formaldehyde) for the polyvinyl alcohol resin film. The casing then is guided by rollers out of tank 160 to the entrance to dryer 154 where it passes between rollers 155 and 156 which, in conjunction with rollers 158 and 159 at the exit end of dryer 154, inflate the casing 128 by air pressure to form an enlarged trapped bubble of air as indicated at 157 to place the casing in a condition in which it can be dried without excessive shrinkage occurring. In dryer 154, the casing is heated by air circulated through line 171 from heater 170 by pump 172. From dryer 154, the casing passes to storage reels (not shown).

While the arrangements for preparing polyvinyl alcohol resin coated and impregnated fibrous casing via the resin solvent application techniques shown in Figs. 2 and 3 have the advantage of utilizing more or less standard equipment for the manufacture of cellulosic fibrous casings, the apparatus and procedures shown in Figs. 4-9 have the advantage of higher speed operation. In Figs. 4-9 of the drawings, there are shown several different 20 embodiments of flat web coaters for coating and impregnating a fibrous saturating tissue web with a polyvinyl alcohol resin solution and drying means for same. In each case, the coated web, immediately or after storage is on reels, is slit to size and formed into tubular casing using conventional apparatus for forming and seaming longitudinally seamed tubes. The casing may be formed and seamed using any conventional adhesive for a polyvinyl alcohol resin film. Such adhesives include molten plasticized polyvinyl alcohol resins of high OH D.S., e.g., above about 80%, polyvinyl alcohol resin aqueous or organic solvent solutions, or reactive 30 adhesives such as isocyanate, epoxy or similar adhesives constituting aqueous or organic solutions of di- or polyfunctional materials, such as those listed above, which cross-link polyvinyl alcohol resins.

In Fig. 4, there is illustrated a knife over roll type coater for use in applying polyvinyl alcohol resin solutions to a fibrous web in accordance with this invention. A fibrous web 235, preferably a long fiber hemp paper or other saturating tissue, is fed over coating roll 236. A viscous solution of polyvinyl alcohol resin is applied to the upper surface of the web as indicated at 238 and metered by coating knife 237. The resultant coated and impregnated web passes through dryer 239 where the polyvinyl alcohol resin is thoroughly dried to a film and cured 10 and may be moisture equilibrated by introduction of moisture at a selected portion of the outlet end of the dryer. Alternatively, the coated, dried and cured web coming out of dryer 239 may be subjected to a separate moisture equilibration step prior to reeling.

In Fig. 5, there is illustrated a floating doctor blade or air knife type coater for application of polyvinyl alcohol resin to a fibrous saturating tissue web. Fibrous web 240 is passed over support channel 241 and idler roll 242. A floating doctor blade or air knife 243 is positioned between channel 241 and 20 roll 242 and meters a viscous polyvinyl alcohol resin solution 244 onto web 240. The thus coated and impregnated web 240 is then passed through dryer 245 where the resin is thoroughly dried to a film, cured, and preferably re-equilibrated with moisture. If desired, the moisture equilibration may be carried out in a separate step after the dryer. The floating doctor blade or air knife coater is operative primarily at low speed coatings and impregnation of nonwoven webs because of the relatively low wet strength of the web. This type coater is more effective for woven fabrics or for nonwoven webs which have been provided with 30 a substantial loading of a wet strength additive.

In Fig. 6, there is shown a modified type of floating doctor blade or air knife coater known as a continuous blanket knife coater. This apparatus is applicable to coating and impregnating

nonwoven webs at higher speeds since the web is supported at the point of application of the coating liquid and the doctor blade. In Fig. 6, the nonwoven saturating tissue web 246 is introduced over idler roll 247. The apparatus includes idler roll 248 and drive roll 249 over which there is fed a continuous belt or blanket 250 for supporting the web being coated. Web 246 is supported by blanket 250 at the point of application of a viscous polyvinyl alcohol resin coating solution 252 which is doctored onto the web by doctor blade or coating knife 251. The coated and impregnated web is passed through dryer 253 where it is dried, cured, and preferably moisture equilibrated. If desired, the re-equilibration with moisture may take place in a separate step following the dryer.

In Fig. 7, there is shown a conventional three-roll, reverse roll coater used here for applying polyvinyl alcohol resin solution to a fibrous web. In this coater, fibrous web 254 is passed over a support roll 255 which is arranged for vertical adjustment to control thickness of coating applied. Adjacent to support roll 255 there is positioned a variable speed transfer roll 256 and doctor roll 257 which is preferably provided with a micrometer adjustment for controlling thickness of film. Doctor roll 257 is provided with a cleaning knife 259 and transfer roll 256 is provided with cleaning knife 260. The viscous coating solution is introduced between rolls 256 and 257 as shown at 258. In this apparatus, the coating material 258 is applied in a control thickness to transfer roll 256, the thickness being controlled by doctor roll 257. The coating from transfer roll 256 is transferred to web 254 which then passes into dryer 261. In dryer 261, the coated and impregnated web is thoroughly dried and cured and preferably re-equilibrated with moisture. If desired, the moisture equilibration may be carried out in a separate step beyond the dryer.

In Fig. 8, there is shown a conventional four-roll reverse roll coater, also known as a contracoater, which can be employed

in the present invention for applying polyvinyl alcohol resin solution to a fibrous web. The fibrous web 262 is fed over an idler roll 263 and around transfer roll 264. The apparatus includes a container 265 for the coating solution 266, viz. a viscous aqueous or organic solvent solution of polyvinyl alcohol resin. A fountain roll 267 is arranged to pick up coating solution 266 and apply it to a transfer roll 268. Adjacent to transfer roll 268 there is positioned a metering roll 269 which controls the thickness of film layer on transfer roll 268 for application 10 to the fibrous web 262. Metering roll 269 is provided with doctor blade 270 for cleaning the surface thereof. After the web is coated by transfer roll 268, the coated and impregnated web passes into dryer 271 where it is thoroughly dried and cured and preferably re-equilibrated with moisture. If desired, the cured polyvinyl alcohol resin film-impregnated web may be re-equilibrated with moisture in a separate conditioning step subsequent to the dryer.

In Fig. 9, there is shown a three-roll direct roll coater for applying polyvinyl alcohol resin solution to a fibrous web. 20 In this apparatus, the fibrous web 272 passes over guide roll 273 and around drive roll 274. The apparatus is provided with a container or receptacle 275 in which the coating solution 276, viz. a viscous aqueous or organic solvent solution of polyvinyl alcohol resin, is positioned. Fountain roll 277 is positioned in coating solution 276 and is arranged upon rotation to apply the coating solution to transfer roll 278 which applies it to the surface of web 272 as the web passes around drive roll 274. The resultant coated and impregnated web is passed into dryer 279 where it is thoroughly dried and cured and preferably is re-equilibrated with 30 moisture. If desired, the moisture re-equilibration may take place in a separate treating step subsequent to the dryer.

Referring to Fig. 10 of the drawings, there is shown a dia-grammatic view of an apparatus for coating or impregnating a

fibrous web with melt-extruded polyvinyl alcohol resin and directly forming the same into a fibrous casing in accordance with this invention.

In Fig. 10, as in the above-described methods, a ribbon of paper 11, passes from roll 12 over rollers 13 and 14 and around formers 15 and 16 which cooperate to form the paper into a longitudinal tube. The paper tube then proceeds downwardly and is guided and supported from within by a mandrel 17. Mandrel 17, which is preferably a hollow metal tube, e.g., a steel pipe, has 10 an outside diameter slightly less than the size of the casing to be produced, e.g., 2-7 inches. The length of mandrel 17 is such, e.g., 10-15 feet, that the casing being produced is adequately supported against undesirable collapse and shrinkage during the forming operations and while the resin in the film is undergoing orientation. Mandrel 17 is suitably supported as shown here using an I-beam 18. The paper 11, now shaped into the form of a tube, continues downwardly over mandrel 17, through a ring member 19, and through a resin melt extrusion device 320. Ring member 19, usually formed of metal, has an outside diameter slightly larger 20 than the diameter of the tube-shaped paper passing through it and functions to maintain the paper in tubular form until it reaches resin melt extruder 320.

Extruder 320 generally has a body portion, shown here only diagrammatically, through which plasticized resin fed thereto is advanced by suitable means such as a rotating single-threaded constant-pitch polyethylene screw and heated in one or more stages to above its melting temperature. At its end adjacent the paper tube, the die portion of extruder 320 defines an annulus surrounding and through which the tube-shaped paper centrally passes. A 30 continuous tubular film of resin issues from extruder 320 through an annular opening 322 located circumferentially of the inner wall 321 of the annulus of extruder 320. In some instances temperatures of resin exiting the die may be more closely regulated by

supplementally heating or cooling the resin immediately adjacent die opening 322 such as at annular surface 321 by conventional heat exchange means, e.g., embedded coils and the like, not shown here. The extruded resin is flowable (i.e., above the second order transition temperature) and under sufficient pressure as it issues inwardly from extruder 320 and upon the surface of the paper tube to effect an impregnation and coating of the fibrous web with a continuous film of polyvinyl alcohol resin.

10 The impregnation and coating operation is aided by the web tube being supplementally supported from within in the zone immediate and adjacent to extruder 320 by a rigid ring member 339 having a diameter slightly larger than the casing to be prepared and which is shrunk onto or otherwise rigidly fitted around mandrel 17. A number of slip rings 323 which also are fixed, such as by shrinking, onto mandrel 17 at suitable intervals, e.g., three feet, function to keep the inside wall of the impregnated and coated web from scraping against mandrel 17 until the resin is suitably set.

20 After extrusion and placement of the polyvinyl alcohol resin film on the web, the web is cooled in a cooling chamber 324. The cooling medium employed is air which enters chamber 324 through an air cooler 326 at line 325 under the influence of blower 327. The cooling in chamber 324 accomplishes two purposes. One function is to preclude the material of the reinforcing paper web from being degraded by heat from the resin film. Cooling also lowers the temperature of the resin film in and on the web below the second order transition point to effect a setting of the deposited film.

30 Mandrel 17 extends into a container 328 containing a solution 329 of a cross-linking agent, such as formaldehyde. In container 328 the impregnated and coated web now in the form of a tubular fibrous casing picks up sufficient cross-linking agent for completion of the insolubilization of the resin in the casing

# 931448

during subsequent curing. Solution 329 optionally also may contain other adjuvants desired to be impregnated into the resin film such as accelerators for the cross-linking agent, additional amounts of plasticizer, dyes, antioxidants, etc.

By passage over a roll 330 located in the bottom of container 328 the tubular casing is collapsed into a ribbon 331 which is then suitably guided by a series of rollers to a drying and curing chamber 333. Through the cooperative effort of a series of rollers 334 and 335 located adjacent the entrance of dryer 333 and 10 a similar series 337 and 338 at the dryer exit, in dryer 333 the casing contains a trapped "bubble" and is maintained in an inflated form 336 for a more uniform curing treatment and to guard against undesired shrinkage. The casing receives sufficient heat treatment in dryer 333 from conventional direct (e.g., hot air) or indirect (e.g., irradiation heat) heating means to cross-link and further insolubilize the polyvinyl alcohol resin film and produce a finished casing.

In the apparatus and operation of the embodiment of the present invention depicted in Fig. 11 of the accompanying drawings, a film-forming and melt-extrudable polyvinyl alcohol resin is suitably mixed with a plasticizer therefor, and the resultant plasticized resin mixture is melt-extruded in a conventional manner to form a substantially flat resin film 342. A web of saturable paper fibers 341 is unwound from a storage reel 340 and guided into face-to-face surface contact with resin film 342. Resin film 342 at this point in the process has cooled somewhat but is still above the second order transition temperature of the resin mixture and hence is flowable when deformed. Reinforcing web 341 and resin film 342 in surface-to-surface contact are then 20 passed through the nip of a pair of rollers 343 and 344 which exert sufficient pressure on the web-film laminate to force the polyvinyl alcohol resin into the pores of the fibrous reinforcing web and produce a resultant article 345 wherein the reinforcing

web is impregnated and coated with a continuous film of the polyvinyl alcohol resin. One or both of rollers 343 and 344 are cooled by conventional means, not shown, so that desired cooling of the polyvinyl alcohol resin to protect the fibrous web material and to set the impregnated resin film may be effected simultaneous with the film impregnation operation.

Resin-reinforced sheet 345 then is slit and cut to the desired width for casing formation by a conventional knife means 346, and the excess is removed by suitable means, here depicted by a 10 passage over a deflecting set of roller guides 349 and 350. The trimmed resin-reinforced sheet 348 is then guided through container 351 holding a bath solution 352 of a cross-linking agent and any other adjuvants desired to be incorporated into the ultimate casing.

Fibrous-reinforced sheet 348 is guided out of bath 352 by rollers 353 and 354 and passed over former 355 which is of the conventional type which folds and forms sheet 348 into the form of a tube. A conventional adhesive applicator 357 is positioned with respect to former 355 to cooperate therewith and apply adhesive 356 to the sheet as the edges are overlapped in the forming operation. The forming and adhesive-application operation thus forms a casing 358 having a continuous longitudinally extending and adhesively bonded seam. 20

Treatment and insolubilization of the casing is completed in a dryer 359 in which the casing is subjected to a curing heat treatment during which cross-linking of the polyvinyl alcohol resin and any needed setting of the adhesive are completed. For maximum efficiency and uniform results in curing heater 359, a "bubble" can be trapped within the casing and the casing maintained 30 in an inflated form 362 by the cooperation of rollers 360 and 361 adjacent the dryer's entrance and rollers 363 and 364, at the exit. If the adhesive 356 employed in seaming the casing is slow-acting, inflation of the adhesive in heater 359, of course, may be desired

to be omitted to avoid disrupting the seam. In addition to using fast-acting seaming adhesives, such problems can be eliminated by postponing the application and/or curing of the cross-linking agent until after a seamed casing has been formed and the seaming adhesive thereof is cured in a separate heating step.

PREPARATION OF POLYVINYL ALCOHOL RESIN FIBROUS CASINGS

A series of experiments were carried out in which a fibrous web was coated and impregnated with film-forming polyvinyl alcohol resins and formed into a fibrous casing. In these experiments, 10 different web impregnation techniques, different polyvinyl alcohol resin compositions, different plasticizers, and different cross-linking agents were used to demonstrate the range of operability of the invention.

The following nonlimiting examples are illustrative of the scope of this invention.

Example 1

In this example, a fibrous sausage casing is prepared directly by impregnating and coating a fibrous paper with an aqueous polyvinyl alcohol resin solution and subsequently evaporating the 20 water from the impregnated web.

A 10% copolymer aqueous solution is prepared using a polyvinyl alcohol/polyvinyl acetate copolymer having an OH group content of 99.5% and a D.P. of about 1600. The polyvinyl alcohol copolymer is dissolved in the solvent mixture at about 90-95°C. To this viscous solution, after cooling, there is added 2.25% glycerol as a copolymer plasticizer, 0.4% formaldehyde as a copolymer cross-linking agent, and 0.22% lactic acid as a catalyst for the cross-linking agent.

A ribbon of 15-lb. Dexstar long fiber hemp paper is removed 30 from a storage roll and passed through an apparatus as shown in Fig. 2 and as described above. The paper is formed into a tube and the viscous polyvinyl alcohol resin solution is introduced through annular die 20 to saturate and coat the paper tube. Resin

solution is applied at a rate corresponding to provide a wet tube thickness of about 50 mils. As the tube passes downward through dryer 23, it is dried in air heated to 120°C. An air stream containing water vapor is withdrawn from dryer 23 and the water can be condensed in a solvent recovery area removed from the dryer as described above. The tube then passes into curing oven 29 where it is cured at 140°C. to effect a thorough cross-linking of the film and to collapse the film to effect hydrogen bonding between substituents of the polyvinyl alcohol copolymer molecules. After 10 curing, the polyvinyl alcohol copolymer casing is subjected to a humid atmosphere to remoisten the casing for flexibility and ease of handling.

After drying and moisture equilibration (to about 12%) under controlled humidity conditions, the casing has a thickness of about 4-6 mils. When the casing is rewet by soaking in water, it swells to a thickness of about 6-8 mils. The casing has greater break strength and displays less elongation at break as compared to fibrous reinforced regenerated cellulose casing. The casing has a break strength of 17-21 lb./in. and an elongation at break of 20 about 15-30% (as compared to about 60-70% for fibrous reinforced regenerated cellulose casing).

A polyvinyl alcohol copolymer-fibrous casing prepared as described above is first soaked in hot water and then stuffed with a bologna emulsion. The casing is tied at one end with a string and after thorough stuffing is closed at the other end with a Tipper clip. The casing is subjected to a normal cooking and smoking operation. There is no breakage of the casing observed and moisture and smoke penetration are about the same as a conventional fibrous cellulosic casing. The casing shows less than 3/16 in. variation 30 in circumference for a 15-in. circumference casing as measured from end to end of a fully stuffed and processed bologna sausage.

#### Example 2

This example illustrates the production of a synthetic casing by the present invention wherein a fibrous saturating web is

impregnated and coated with an aqueous polyvinyl alcohol resin solution and the resultant resin-coated web is formed into a tube in a seaming operation.

A 10% solution of a polyvinyl alcohol/polyvinyl acetate copolymer having an OH group D.S. of 98% and a D.P. of about 1400 and containing 2.25% glycerol, 0.4% formaldehyde, and 0.22% lactic acid is prepared following the general procedure described in Example 1. The viscous polyvinyl alcohol copolymer solution thus prepared is applied to a 15-lb. Dexstar long fiber hemp paper on a knife over roll coater as shown in Fig. 4 and described above to provide a coated and impregnated paper having a wet thickness of about 50 mils and the coated web is dried under conditions similar to those used in Example 1. When dried, the paper has a thickness of about 4-6 mils. The paper has a rewet thickness of about 6-8 mils and a rewet strength and an elongation at break characteristics superior to corresponding cellulose impregnated paper.

The impregnated, dried and cured paper is equilibrated with sufficient moisture to render it flexible and easy to handle by passing through a humid atmosphere. The impregnated paper is slit to the desired size, for any particular casing, and is formed into a continuous tube on a standard sealer for forming longitudinal seams in the manufacture of tubing. In the manufacture of this tubular casing, a 10% aqueous solution of polyvinyl alcohol/polyvinyl acetate copolymer (OH group D.S. of about 99.5), plasticized with glycerol and containing formaldehyde and lactic acid, in the same proportions as the impregnating solution, is applied as a seaming adhesive. As the adhesively seamed joint is formed, the casing is heated to dry the adhesive and effect thorough cross-linking both within the adhesive to the surface being adhered.

30 The casing which is formed does not tend to break across the seam when subjected to routine tensile tests.

The fibrous casing prepared in this example has strength and processing properties similar to the casing of Example 1.

Examples 3-10

These examples illustrate further embodiments of synthetic casings of the present invention produced by impregnating and coating a flat stock of a saturating web with an aqueous solution of polyvinyl alcohol resin, drying the treated web, and forming the resin-impregnated web into a tube in a seaming operation.

Following the general procedure of Example 2, 10% aqueous solutions of film-forming polyvinyl alcohol resins containing glycerol and cross-linking agents are prepared and coated onto flat webs of 15-lb. Dexstar long fiber hemp paper and the resin-saturated webs are dried and then formed into tubes in a seaming operation, except that the polyvinyl alcohol resins and cross-linking agents in the web impregnating aqueous resin solutions, the web coating apparatus, and the seaming adhesives utilized are as indicated in Table 1 below.

Table 1

Example	Impregnating Aqueous Resin Solution Composition		Cross-Linking Agent System	Web Coater	Tube Seaming Adhesive
	Polyvinyl Alcohol Resin	Resin <sup>✓a</sup>			
3	PVA/PVAC (OH D.S., 88%; D.P., 1500)	0.4% formaldehyde 0.22% lactic acid		Floating doctor blade coater (Fig. 5)	Same as impregnating resin solution
4	PVA/PVAC (OH D.S., 86%; D.P., 1700)	do.		Blanket knife coater	do.
5	PVA/PVAC (OH D.S., 99%; D.P., 1800)	0.4% formaldehyde 0.3% malic acid		Three-roll reverse roll coater (Fig. 7)	30% 2,4-toluene diiso- cyanate in acetone
6	do.	1.25% trimethylol melamine 0.2% citric acid		Three-roll direct roll coater (Fig. 9)	30% cyanoacrylate ester in acetone
7	do.	0.5% polyamide epi- chlorohydrin (Kymene 557)		Four-roll reverse roll coater (Fig. 8)	30% butadiene diepoxide in acetone
8	do.	1.0% dimethylol urea 0.2% lactic acid		do.	Same as impregnating resin solution
9	do.	5% glyoxal 0.3% malic acid		do.	do.
10	do.	5.5% glutaraldehyde 0.2% malic acid		do.	do.

<sup>✓a</sup> Polyvinyl alcohol/polyvinyl acetate copolymer.

The seamed fibrous-reinforced polyvinyl alcohol resin film casings of Examples 3-10 all possess strength and processing properties similar to the casings of Examples 1 and 2.

All of the above examples utilize glycerol as the plasticizer for the polyvinyl alcohol resin film of the casings produced. It will be understood, however, that similar superior casings are produced by substituting, for glycerol in the procedures of the above examples, an effective amount, e.g., from about 0.5% to about 4%, of any of the other hereinabove described water-soluble, monomeric or polymeric hydroxyl, amino, or amide group-containing polyvinyl alcohol resin plasticizing agents.

Example 11

This example illustrates an embodiment of the invention wherein a synthetic casing is directly produced by impregnating and coating a saturating fibrous web with an organic solvent solution of polyvinyl alcohol resin and evaporating the solvent.

The procedure of Example 1 is repeated with the exception of substituting, for water as the impregnating resin solution solvent, a 30:70 (V/V) mixture of methanol and water.

20 The resultant directly produced fibrous-reinforced polyvinyl alcohol resin casing has strength and processing characteristics similar to the casings of the preceding examples.

Examples 12-16

These examples illustrate embodiments of the invention wherein a synthetic casing is produced by saturating a flat web of a saturating fibrous paper with an organic solvent solution of polyvinyl alcohol resin, drying the resin-solution saturated web, and forming the resultant resin impregnated and coated web into a tubular casing in a seaming operation.

30 Following the general procedure of Example 2, 10% organic solvent solutions of film-forming polyvinyl alcohol resins containing glycerol and cross-linking agents are prepared and coated onto flat webs of 15-lb. Dexstar long fiber hemp paper, and the

931448

resin-saturated webs are dried and then formed into tubular casings in a seaming operation, except that, in these runs, the web coating apparatus, the seaming adhesives, and the polyvinyl alcohol resins, cross-linking agents, and solvents in the web impregnating solutions utilized are those indicated in Table 2 below.

Table 2

Example	Impregnating Resin Solution Composition			Web Coater	Tube Seaming Adhesive
	Polyvinyl Alcohol Resin	Cross-Linking Agent System	Solvent		
12	PVA/PVAc (OH D.S., 88%; D.P., 1200)	0.4% formaldehyde 0.22% lactic acid	Methanol/water, 30:70 (V/V)	Floating doctor blade coater (Fig. 5)	Aqueous PVA/PVAc solution (Ex. 2)
13	PVA/PVAc (OH D.S., 70%; D.P., 1500)	do.	Methyl ethyl ketone	Blanket knife coater (Fig. 6)	do.
14	PVA/PVAc/PMA <sup>a</sup> (OH D.S., 50%; D.P., 1400)	0.4% formaldehyde 0.3% malic acid	Methyl acetate	Three-roll reverse roll coater (Fig. 7)	30% 2,4-toluene diisocyanate in acetone
15	PVA/PVAc (OH D.S., 99.5%; D.P., 1000)	1.25% trimethylol melamine 0.2% citric acid	Methanol/water, 30:70 (V/V)	Three-roll direct roll coater (Fig. 9)	30% diketene of dimerized linoleic acid in acetone
16	PVA/PVAc (OH D.S., 30%; D.P., 1800)	0.5% glutaraldehyde 0.2% malic acid	Benzene	Four-roll reverse roll coater (Fig. 8)	30% butadiene diepoxide in acetone

<sup>a</sup>Terpolymer having a carboxylic group D.S. of about 5% obtained by hydrolyzing polyvinyl acetate/poly(methacrylate acid copolymer.

The seamed fibrous-reinforced polyvinyl alcohol resin casings produced in Examples 12-16 have strength and processing properties similar to the casings of the preceding examples.

Again, while glycerol is the polyvinyl alcohol resin plasticizer utilized in the production of the casings of Examples 11-16, it will be understood that casings of comparable characteristics are produced by substituting in the procedures of these examples effective amounts of any of the other resin solvent-soluble monomeric or polymeric polyvinyl alcohol resin plasticizing compounds 10 hereinabove described.

Example 17

This example illustrates the direct preparation of a synthetic casing in accordance with the present invention using an aqueous solution of a polyvinyl alcohol resin and resin insolubilization by coagulation to impregnate and coat a fibrous saturating web.

An aqueous 10% polyvinyl alcohol resin solution is prepared of a polyvinyl alcohol resin having an OH group D.S. of 99.5% and a D.P. of about 1100 following the procedure of the preceding examples, excepting the addition of a plasticizer and a cross-linking agent system is omitted. 20

The viscous 10% polyvinyl alcohol copolymer solution thus prepared is applied to a 15-lb. Dexstar long fiber hemp paper in an apparatus as shown in Fig. 3 and described above wherein the paper is formed into a tube, and the resin solution is applied to the tube through annular die 20 to provide a wet tube thickness of about 50 mils. The polyvinyl alcohol resin is insolubilized in coagulating baths 124 and 131 consisting of aqueous solutions containing 5% concentrated (100%) sulfuric acid and 15% sodium sulfate. 30 The resultant tube then is passed through water baths 141 and 151 for rinsing and then through bath 161 constituting an aqueous solution comprising 30% glycerol, 1% formaldehyde, and 0.2% lactic acid. From bath 161, the tube is passed through dryer 154 where cross-linking and drying are completed.

Casing which has a thickness of about 4-6 mils is equilibrated with sufficient moisture to render it flexible and easy to handle. Rewet in water, the casing swells to a thickness of 6-8 mils. It has greater heat strength, displays less elongation at break than conventional reinforced cellulose casing, and performs adequately when stuffed, cooked, and smoked as described in Example 1.

Example 18

This example illustrates an embodiment of the present invention wherein a synthetic casing is directly prepared by saturating a fibrous web formed into a tube with an organic solvent solution of polyvinyl alcohol resin and subsequently insolubilizing the polyvinyl alcohol resin as a film in a regeneration bath.

The general casing preparation procedure of Example 17 is repeated with the exceptions of (a) in the impregnating 10% resin solution preparation, substituting a 30:70 (V/V) methanol-water mixture as the resin solvent, and (b) in coagulating baths 124 and 131, substituting acetone.

The resultant casing produced, similar to those of the preceding examples, has greater strength and shows less elongation at break than conventional fibrous reinforced cellulose casing, and performs suitably when stuffed, cooked, and/or smoked as hereinabove described in Example 1.

Example 19

This example illustrates the direct preparation of synthetic casing in accordance with the present methanol using an aqueous alkaline solution of an alkali soluble, film-forming polyvinyl alcohol resin.

The general casing preparation procedure of Example 17 is repeated with the exceptions of (a) in the impregnating 10% resin solution preparation, substituting as the polyvinyl alcohol resin component a polyvinyl alcohol/polyvinyl acetate copolymer having an OH group content of about 50% and a D.P. of about 1600 and, as

the polyvinyl alcohol resin solvent, an aqueous 4% solution of sodium hydroxide, and (b) in bath 141, substituting dilute (1%) aqueous sulfuric acid solution.

The resultant fibrous-reinforced polyvinyl alcohol resin casing produced has similar strength and processing characteristics as the casings of the preceding examples.

Examples 20-27

These examples illustrate additional embodiments of the present invention wherein synthetic casings are produced using aqueous alkaline solutions of polyvinyl alcohol resins.

The general casing preparation procedure of Example 19 is repeated with the exceptions of utilizing in the 10% resin-containing, web-impregnating solutions and in the glycerol plasticizing-containing bath (161), the compositions indicated in Table 3 below.

Table 3

Example	Web Impregnating Solution Composition			Cross-Linking Agent System in Plasticizer Bath
	Polyvinyl Resin	Alcohol	NaOH Conc. %	
20	PVA/PVAc (OH D.S., 50%; D.P., 1600)	3	None	None
10	21 PVA/PVAc (OH D.S., 40%; D.P., 1700)	8	do.	do.
22	PVA/PVAc/PA <sup>a</sup> (OH D.S., 50%; D.P., 1300)	4	do.	do.
23	PVA/PVAc/PA <sup>b</sup> (OH D.S., 30%; D.P., 1800)	do.	do.	do.
20	24 do.	do.	do.	1% trimethylol melamine 0.3% malic acid
25	PVA/PVAc/PMA <sup>c</sup> (OH D.S., 50%; D.P., 1300)	do.	do.	None
26	PVA/PVAc (OH D.S., 40%; D.P., 1700)	do.	do.	1% trimethylol melamine 0.3% malic acid
27	do.	do.	0.2% methylol melamine	None

<sup>a</sup>Terpolymer containing 0.5% acrylate obtained by hydrolyzing poly-vinyl acetate/polyacrylic acid copolymer.

<sup>b</sup>Terpolymer containing 8% acrylate obtained by hydrolyzing poly-vinyl/polyacrylic acid copolymer.

<sup>c</sup>Terpolymer of carboxylate content of about 3% obtained by hydrolyzing polyvinyl acetate/maleic acid copolymer.

All of the resultant casings produced, similar to those of the preceding examples, have suitable processing characteristics and elongation properties superior to conventional fibrous-reinforced cellulose casings.

#### 40 Example 28

This example illustrates the preparation of synthetic casing in accordance with the present invention wherein a flat web

of a fibrous paper is saturated with an aqueous alkaline solution of a polyvinyl alcohol resin, the resin is regenerated on the flat web, and the resin coated and impregnated web is formed into a tubular casing in a seaming operation.

A 10% alkaline solution of 50% OH D.S. polyvinyl alcohol/polyvinyl acetate copolymer is produced as described in Example 20 and then applied to a flat web of 15-lb. Dexstar long fiber hemp paper on a four-roll reverse coater as shown in Fig. 8 and as described above. The resultant coated and impregnated paper is 10 then passed through a sequence of coagulation, wash, and plasticizing baths of the compositions employed in Example 20. The resultant resin-impregnated and coated web is then formed into a tube having a longitudinally extending adhesive seam on a sealer using an aqueous polyvinyl alcohol resin solution adhesive as in Example 2.

The resultant casing has strength and processing properties similar to the casings of the preceding examples.

In the above examples, aqueous 3-8% sodium hydroxide solutions are used to dissolve the alkali-soluble polyvinyl alcohol 20 resins. It will be understood that effective amounts of aqueous solutions of other alkalis, e.g., KOH, NH<sub>4</sub>OH, and (CH<sub>3</sub>)<sub>4</sub>NOH, when substituted for sodium hydroxide solutions in the procedures of the applicable examples produce polyvinyl alcohol resin casings of comparable properties. In general, the concentration of alkali in such aqueous solutions may vary from about 1 to about 20%. Similarly, substitution of effective coagulation baths of varied acid and salt contents in such examples (as well as the other examples, using coagulation for resin insolubilization) can be carried out to produce casings of the present invention. In general, effective resin coagulation and regeneration baths are those having a pH and salt content equivalent to aqueous solutions containing 30 1-20% H<sub>2</sub>SO<sub>4</sub> and an amount of Na<sub>2</sub>SO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ranging from about 5% to saturation levels (e.g., 40%).

Example 29

This example illustrates the use of melt-extruded polyvinyl alcohol resin in the direct production of synthetic casing by the present invention.

One hundred parts by weight of a dry polyvinyl alcohol/polyvinyl acetate copolymer having an OH group D.S. of about 71% and having a 4% aqueous solution viscosity of about 11 centipoises at 20°C. are uniformly mixed with 20 parts by weight of Pycal 94, a polymeric plasticizer for polyvinyl alcohol which is a polyoxy-10 alkylene phenolic ether containing an average of five ethylene oxide units per molecule. The moisture content of the mixture is less than about 0.1% by weight.

A ribbon of 15-lb. Dexstar long fiber hemp paper is removed from a storage roll and passed through an apparatus as shown in Fig. 10 and as described above. The paper is formed into a tube and polyvinyl alcohol copolymer is melt-extruded (exit temperature about 175°C.) through annular die 320 to saturate and coat the paper tube. Copolymer is applied at a rate corresponding to provide an impregnated and coated tube thickness of about 5-10 mils. 20 The coated tube passes downward and is immediately cooled in cooler 324 by air circulating at about 15°C. The tube then passes into tank 328 where it is contacted with an aqueous solution comprising 1% formaldehyde and 0.2% lactic acid, the latter being a catalyst for the formaldehyde cross-linking agent. The tube then passes through dryer 333 where it is carried at temperatures ranging up to 140°C. to effect a thorough cross-linking and insolubilization of the film. After curing, the resultant casing is exposed to a humid atmosphere, as is conventional, to raise its moisture content to levels, e.g., 10-15% by weight, as is basis, 30 at which flexibility and handling properties are improved.

The casing has greater break strength and displays significantly less elongation at break as compared to fibrous reinforced regenerated cellulose casing.

A polyvinyl alcohol copolymer fibrous casing prepared as described above, after soaking in hot water, is stuffed with a bologna emulsion, and then subjected to a normal cooking and smoking operation. There is no breakage of the casing observed and moisture and smoke penetration are about the same as a conventional fibrous celullosic casing.

Examples 30-41

These examples illustrate further embodiments of the use of melt-extrusion in the direct production of polyvinyl alcohol resin casings by the present invention.

The general procedure of Example 29 is repeated to directly produce additional fibrous polyvinyl alcohol resin sausage casings, excepting the various polyvinyl alcohol resins and plasticizers shown in Table 4 are substituted for those described in Example 29.

Table 4

Exam- ple	Formula	Polyvinyl Alcohol Resin		Ingredient	Plasticizer		Resin Melt (exit) temp., °C.
		OH D.S., %	Group Visc./a cps		Amount Added parts by wt.		
20	32	PVA/PVAc	99.5	10	Pycal 94	20	200
	33	do.	do.	do.	do.	10	205
	34	do.	do.	do.	Carbowax 400/b	15	200
	35	PVA/PVAc	98.0	12	Pycal 94	15	195
	36	do.	do.	do.	Carbowax 300/c	25	195
	37	PVA/PVAc	95	9	Pycal 94	10	200
	38	do.	do.	do.	Pycal 94 Triethylene glycol	10 5	190
	39	PVA/PVAc	85	11	Pycal 94	15	185
30	40	PVA/PVAc	70	12	Glycerol	30	175
	41	PVA/PVAc/ PMAA/d	95	15	Pycal 94	20	190

/a As 4% aqueous solutions at 20°C.

/b Polyethylene glycol having an average molecular weight of about 400.

/c Polyethylene glycol having an average molecular weight of about 300.

/d Terpolymer having a carboxyl group D.S. of about 1% prepared by hydrolyzing to the listed OH D.S. a polyvinyl acetate/polymethacrylic acid copolymer.

The resultant casings produced in Examples 32-41 are similar to that of Example 29. Resins of D.S.'s (OH) of at least 95% produced the best casings.

Example 42

This example shows the production of synthetic casing by the present invention wherein a flat web of a fibrous paper is impregnated and coated by melt-extrusion with polyvinyl alcohol resin and the resin coated web is formed into a tubular casing in a seaming operation.

10 A sample of the plasticized polyvinyl alcohol resin mixture described in Example 30 is extruded at about 200°C. as a flat softened film having a thickness of about 20 mils and the resultant film is then pressed into and through a web of 15-lb. Dexstar long fiber hemp paper by passage of the film and web in face-to-face contact between the nip of two rolls having chilled (10°C.) chrome surfaces as shown in Fig. 11 and described above. The resultant resin impregnated and coated web has a continuous polyvinyl alcohol resin film thickness of about 10 mils. The resultant sheet is slit to a six-inch width and then passed through cross-linking agent 20 bath 352 comprising an aqueous solution of 1% dimethylol urea and 0.2% lactic acid. The treated sheet then is formed into a continuous tube in a seaming operation using an aqueous solution comprising 10% polyvinyl alcohol/polyvinyl acetate copolymer (OH group D.S. - 98%, viscosity - 10 cps), 2% glycerol, 1% formaldehyde, and 0.2% lactic acid as the adhesive. After setting of the seaming adhesive, curing and cross-linking of the resin in the casing is completed in heater 359 at temperatures ranging up to 140°C.

30 The resultant casing which is formed does not tend to break across the seam when subjected to routine tensile tests and otherwise has properties similar to those of the preceding examples.

Examples 43-45

The procedure of Example 42 is repeated excepting 30% acetone solutions of each toluene diisocyanate, butadiene diepoxide,

and the diketene of dimerized linoleic acid, are substituted as the seaming adhesive.

The resultant casings obtained have strength and break properties similar to those of the casing of Example 42.

The paper used in the above examples was a long fiber hemp paper. In general, however, similar results are obtained by substituting in the processes of any of the examples any saturating tissue or nonwoven or woven web of suitable strength. In some cases, a small amount of a surfactant or wetting agent may be 10 added in a preliminary treatment to aid thorough penetration of the polyvinyl alcohol resin into the web.

In the general examples given above, a limited number of compounds are specifically shown as a cross-linking agent for the polyvinyl alcohol resin films formed. Similar results, however, are obtained by substituting in any of the processes of the examples any of the other polyvinyl alcohol resin cross-linking agents specifically listed hereinabove. It further will be understood that a cross-linking agent, where it is employed, may be omitted from use in any of the procedures of the general examples above to produce casings of the present invention. Such an omission, however, as described above, may, and usually does, produce less preferred casings. 20

The casings produced in the processes of the above examples are essentially clear. Similar processes, however, can be utilized in the production of colored casings. Such colored casings, for example, may be produced by incorporating F.D.A. and U.S.D.A. approved pigments or dyes into the starting resin solution or melt and/or into baths in which the resin treated web is treated. In particular, aluminum lake pigments or F.D.A. approved food dyes may 30 be used.

It will be further understood that the invention also embraces the addition to the polyvinyl alcohol resin film coating, usually through an addition to a starting solution or melt, of

minor amounts, e.g., up to about 20% by weight, of other film-forming resins, e.g., polyvinyl acetate, amylose, etc., provided such resins are compatible with the polyvinyl alcohol resin and the solution or extrusion conditions utilized and do not seriously detract from the characteristic strength advantages gained by virtue of the use of polyvinyl alcohol resins as the primary film component.

It further will be understood that the casings produced in accordance with the present invention, in addition to being treated 10 as described above, may be treated during or after the manufacture thereof with other monomeric or polymeric agents designed to coat, impregnate or chemically react, themselves or through cross-linking agents, with the casing material to modify the outside and/or inside surface of the polyvinyl alcohol film of the casing and thereby adapt to the modified casing for specialized uses. In general, such auxiliary agents which can be used in the present invention include those conventionally employed in the treatment of cellulosic casings to impart thereto specially desired gloss, flexibility, strength, shrinkage, adherent, non-adherent, moisture 20 resistant, water-permeability, vapor-permeability, abrasion, abrasion-resistant, anti-mycotic, and the like properties. Especially useful auxiliary agents, in addition to those described above, include inside and/or outside surface-applied lubricants and release agents which may be oils such as silicon oils and polymethyl hydrogen siloxane, fats such as acetylated monoglycerides, C<sub>16</sub>-C<sub>18</sub> fatty ketene dimers, cetyl alcohol, or other compounds such as aluminum sulfate, lactic acid, inositol, methyl cellulose, and carboxymethyl cellulose; inside surface-applied shrinkage and adhesive coating agents which may be proteinaceous 30 such as those provided by gelatin-acetylated monoglyceride mixtures and gelatin cured with dialdehydes such as glutaraldehyde and liquid smoke; and outside surface-applied, water- and vapor-permeability reducing coating materials such as saran (vinylidene

chloride homopolymers and copolymers) and polymeric mixtures of a paraffin wax and a dimerized ester of an epichlorohydrin-bis-phenol reaction product.

The tubular casings produced in accordance with this invention are useful primarily for processing and packaging sausages such as bologna, etc. These casings may also be used for packaging food and other products. The casings are also useful as semi-permeable membranes for purification of water by reverse osmosis and as hemodialysis membranes in artificial kidney machines.

10 Other embodiments which do not depart from the spirit and scope of the present invention, of course, will be apparent to those skilled in the art. Accordingly, it will be understood the present invention is to be limited only by the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A synthetic casing comprising a tube of a fibrous web longitudinally seamed and impregnated and coated with a continuous polyvinyl alcohol resin film, said film resulting from depositing and insolubilizing in and on said fibrous web a film-forming polyvinyl alcohol resin having a degree of substitution with regard to hydroxyl groups of at least about 20%.

2. The synthetic casing according to Claim 1 wherein said film-forming polyvinyl alcohol resin is deposited on said fibrous web by impregnating and coating said fibrous web with a solvent solution of said polyvinyl alcohol resin and contacting the resin solution-impregnated web with a coagulating bath to regenerate said polyvinyl alcohol resin.

3. The synthetic casing according to Claim 2 wherein said web impregnating solution is an organic solvent solution of a film-forming polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 99.99% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

4. The synthetic casing according to Claim 2 wherein said web impregnating solution is an aqueous alkaline solution of an alkali-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 80% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

5. The synthetic casing according to Claim 2 wherein said web impregnating solution is an aqueous solution of a water-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 80% to about 99.99% and a degree of polymerization of at least about 800.

6. The synthetic casing according to Claim 1 wherein said film-forming polyvinyl alcohol resin is deposited on said fibrous web by impregnating and coating said fibrous web with a solvent solution of said polyvinyl alcohol resin and evaporating the solvent from said resin solution-impregnated web.

7. The synthetic casing according to Claim 6 wherein said web impregnating solution is an organic solvent solution of an organic solvent-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 99.99% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

8. The synthetic casing according to Claim 6 wherein said web impregnating solution is an aqueous alkaline solution of an alkali-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 80% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

9. The synthetic casing according to Claim 6 wherein said web impregnating solution is an aqueous solution of a water-soluble

polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 80% to about 99.99% and a degree of polymerization of at least about 800.

10. The synthetic casing according to

Claim 1 wherein said deposited and insolubilized polyvinyl alcohol resin film contains a plasticizer.

11. The synthetic casing according to Claim 1 wherein said polyvinyl alcohol resin deposited on said fibrous web is a plasticized melt extruded film-forming polyvinyl alcohol resin having a degree of substitution with regard to hydroxyl groups of at least 60%.

12. The synthetic casing according to Claim 11 wherein the melt extruded polyvinyl alcohol resin contains up to about 40 parts by weight of a plasticizing agent per 100 parts of said resin and said plasticized resin is essentially moisture free and melts substantially uniformly at a temperature below about 220°C.

13. The synthetic casing according to Claim 1 wherein said insolubilized polyvinyl alcohol resin film contains cross-linkages introduced by reaction of said deposited polyvinyl alcohol resin with a cross-linking agent.

14. The synthetic casing according to Claim 1 wherein said fibrous web is a long fiber hemp saturating tissue.

15. A process for producing a synthetic casing wherein a fibrous web is subjected to resin-coating and tube-forming operations and thereby converted into a fibrous re-enforced synthetic resin tube, characterized by, in the resin coating operation, depositing and insolubilizing a film-forming polyvinyl alcohol resin having a degree of substitution with regard to hydroxyl groups of at least about 20% as a continuous film in and on said fibrous web.

16. The process for producing a synthetic casing according

to Claim 15 wherein said fibrous web is impregnated and coated with said continuous polyvinyl alcohol resin film by impregnating and coating said fibrous web with a solvent solution of said polyvinyl alcohol resin and contacting the resin solution impregnated web with a coagulating bath to regenerate said polyvinyl alcohol resin.

17. The process for producing a synthetic casing according to Claim 16 wherein said web impregnating solution is an organic solvent solution of an organic solvent-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 99.99% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

18. The process for producing a synthetic casing according to Claim 16 wherein said web impregnating solution is an aqueous alkaline solution of an alkali-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 80% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

19. The process for producing a synthetic casing according to Claim 16 wherein said web impregnating solution is an aqueous solution of a water-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 80% to about 99.99% and a degree of polymerization of at least about 800.

20. The process for producing a synthetic casing according

to Claim 15 wherein said film-forming polyvinyl alcohol resin is deposited on said fibrous web by impregnating and coating said fibrous web with a solvent solution of said polyvinyl alcohol resin and evaporating the solvent from said resin solution-impregnated web.

21. The process for producing a synthetic casing according to Claim 20 wherein said web impregnating solution is an organic solvent solution of an organic solvent-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 99.99% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

22. The process for producing a synthetic casing according to Claim 20 wherein said web impregnating solution is an aqueous alkaline solution of an alkali-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 25% to about 80% and a degree of polymerization of at least about 800, said polyvinyl alcohol resin being a polyvinyl alcohol/polyvinyl ester copolymer or a carboxylated polyvinyl alcohol/polyvinyl ester resin having a degree of substitution with regard to carboxyl groups ranging up to about 25%.

23. The process for producing a synthetic casing according to Claim 20 wherein said web impregnating solution is an aqueous solution of a water-soluble polyvinyl alcohol resin characterized by a degree of substitution with regard to hydroxyl groups in the range of from about 80% to about 99.99% and a degree of polymerization of at least about 800.

24. The process for producing a synthetic casing according

to Claim 15 wherein said deposited and insolubilized polyvinyl alcohol resin film contains a plasticizer.

25. The process for producing a synthetic casing according to Claim 15 wherein said polyvinyl alcohol resin deposited on said fibrous web is a plasticized melt extruded film-forming polyvinyl alcohol resin having a degree of substitution with regard to hydroxyl groups of at least 60%.

26. The process for producing a synthetic casing according to Claim 25 wherein the melt extruded polyvinyl alcohol resin contains up to about 40 parts by weight of a plasticizing agent per 100 parts of said resin and said plasticized resin is essentially moisture free and melts substantially uniformly at a temperature below about 220°C.

27. The process for producing a synthetic casing according to Claim 15 wherein said insolubilized polyvinyl alcohol resin film contains cross-linkages introduced by reaction of said deposited polyvinyl alcohol resin with a cross-linking agent.

28. The process for producing a synthetic casing according to Claim 15 wherein said fibrous web is a long fiber hemp saturating tissue.

29. The process for producing a synthetic casing according to Claim 15 in which the casing is formed into a tube at the time of said deposition and insolubilization of said polyvinyl alcohol resin.

30. The process for producing a synthetic casing according to Claim 15 wherein, at the time of said deposition and said insolubilization of said polyvinyl alcohol resin, said fibrous web is in the form of flat stock and the resultant resin impregnated and coated flat stock subsequently is formed into a tube having an adhesively bonded longitudinal seam in a seaming operation.

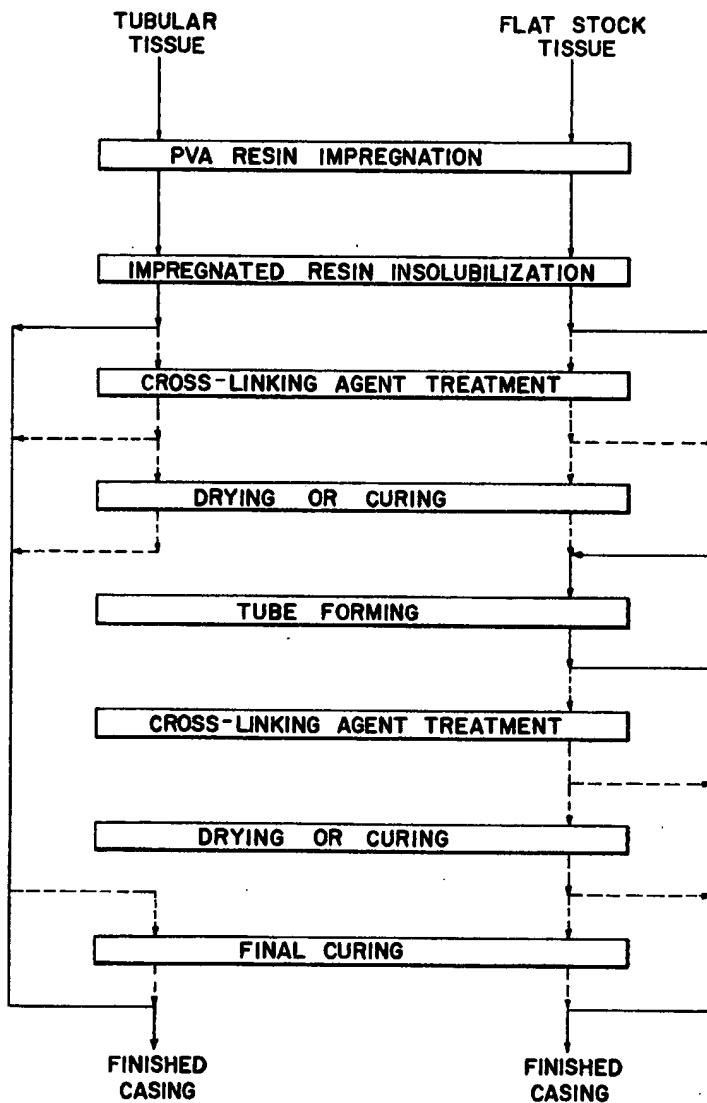


FIG. I

**INVENTORS**  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS

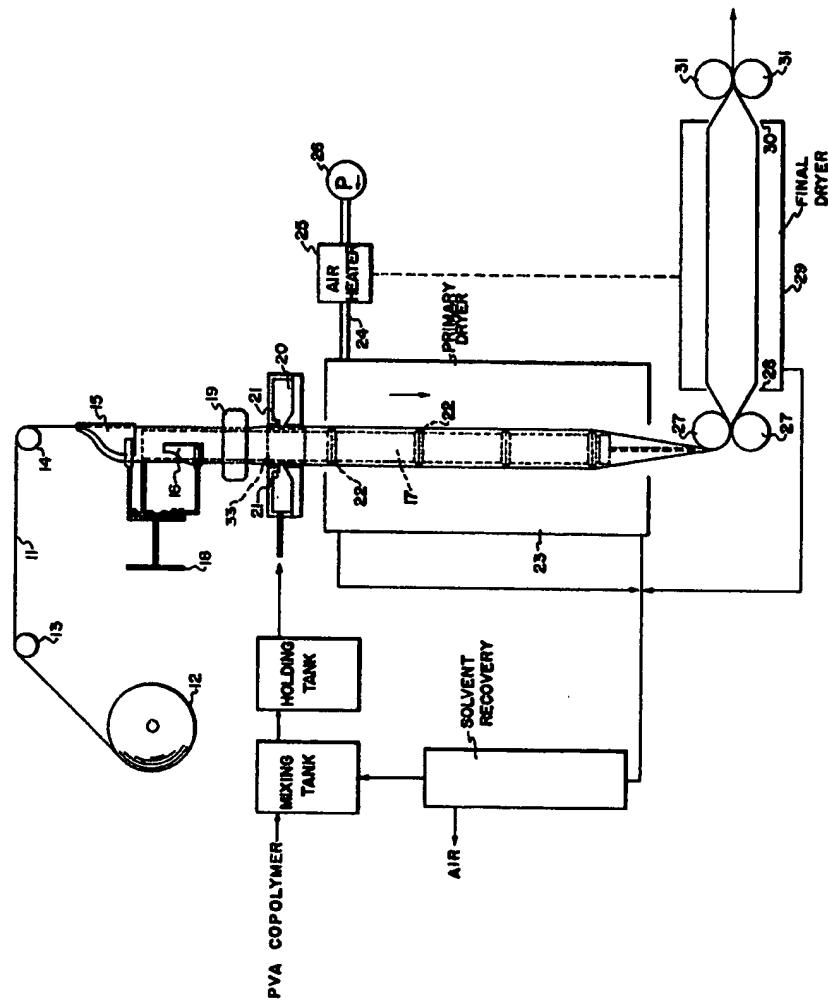


FIG. 2

**INVENTORS**  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

Meredith & Finlayson  
PATENT AGENTS

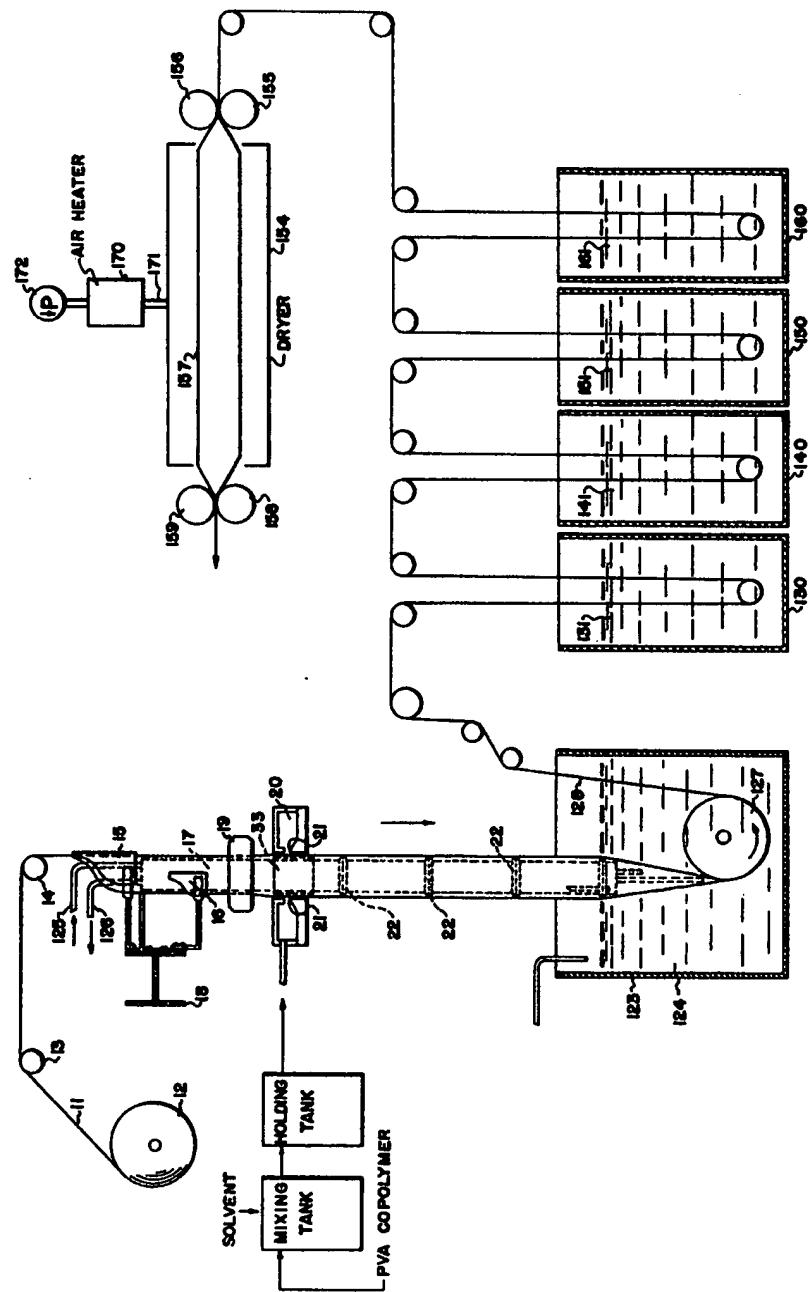
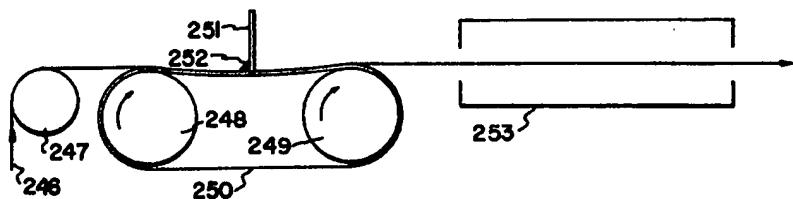
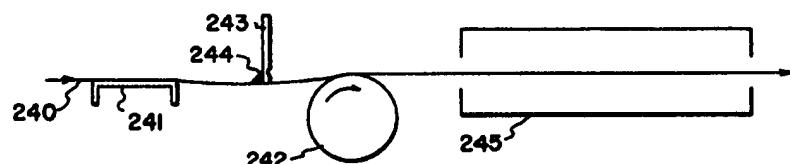
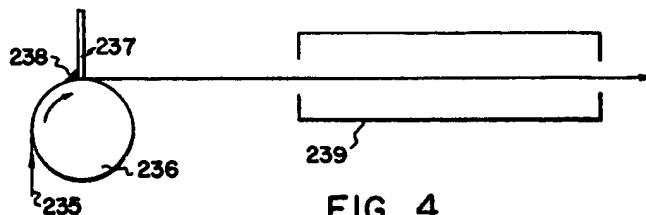


FIG. 3

**INVENTORS**  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS



INVENTORS  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS

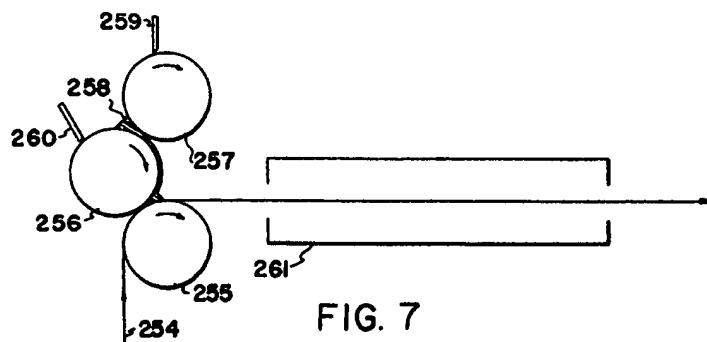


FIG. 7

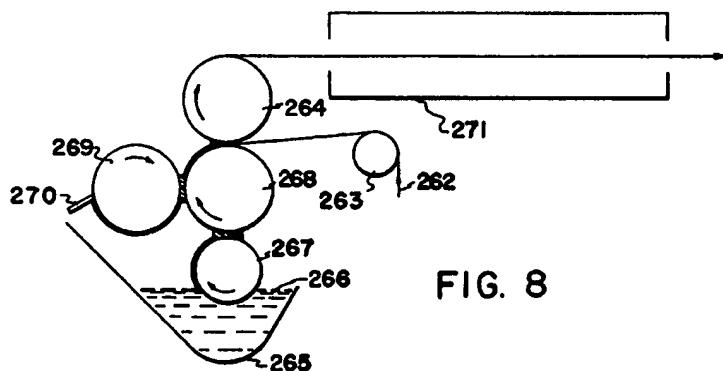


FIG. 8

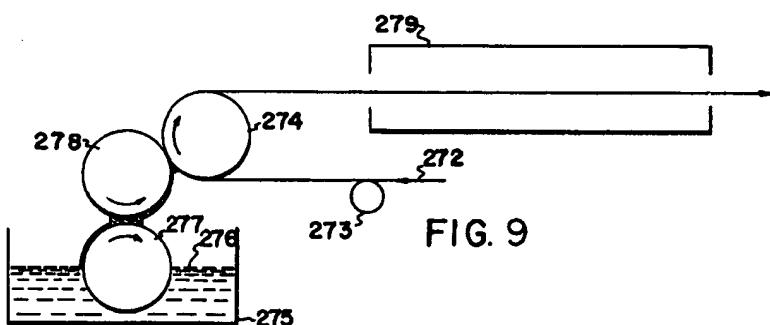
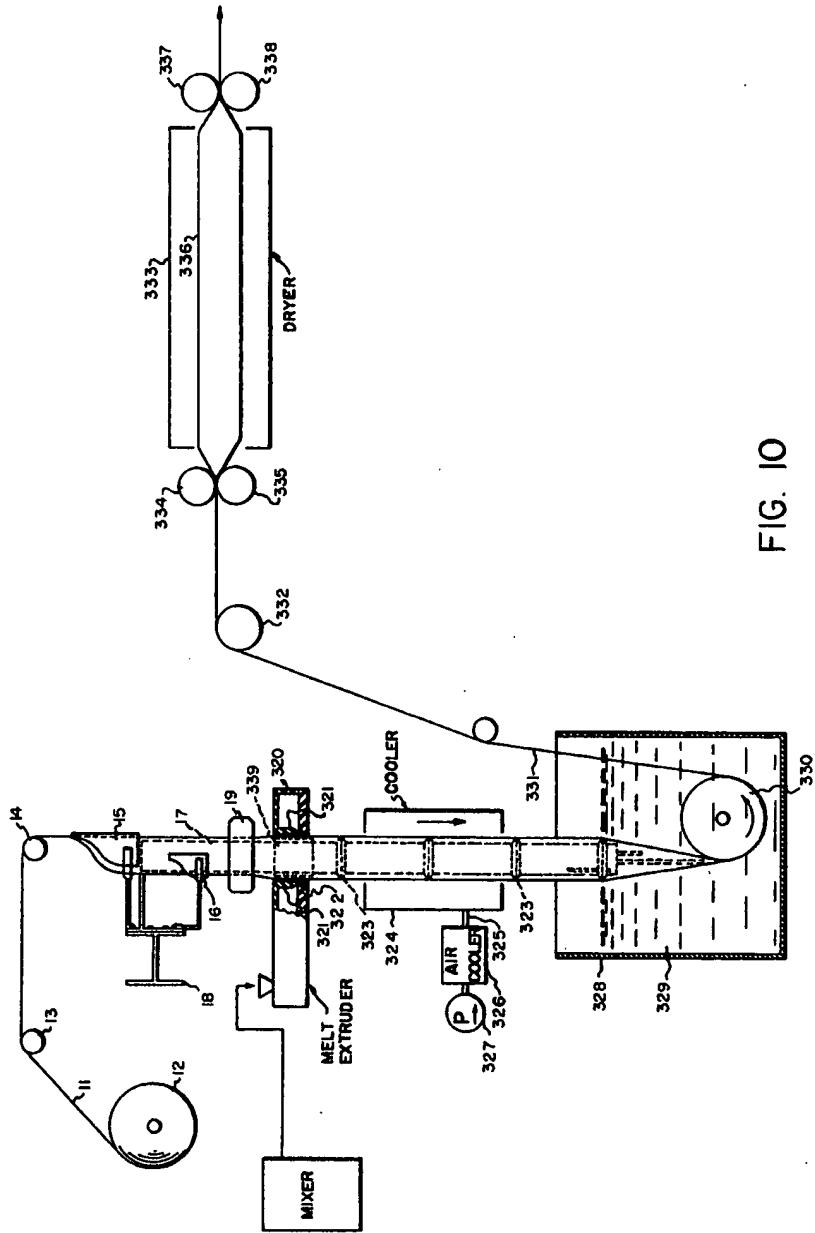


FIG. 9

INVENTORS  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS



INVENTORS  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS

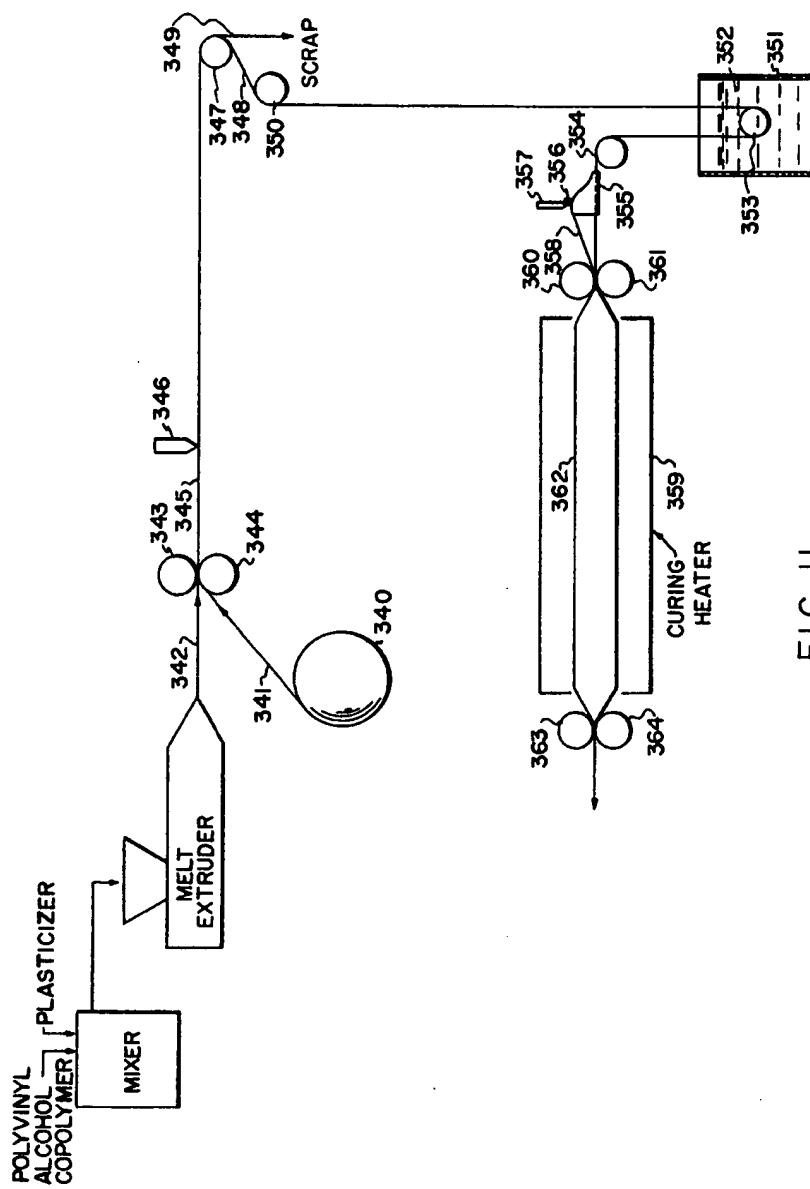


FIG. 11

INVENTORS  
SEYMOUR OPPENHEIMER & ALBIN F. TURBAK

*Meredith & Finlayson*  
PATENT AGENTS

**SUBSTITUTE**

***REPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***